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**ELECTRON RADIATION EFFECTS IN RUBY**

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# ELECTRON RADIATION EFFECTS IN RUBY

by Hubert H. Grimes

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## SUMMARY

The effect of 2-MeV electron bombardment on ruby laser crystals was studied by optical absorption spectroscopy. Except for a new ultraviolet absorption band attributed to aluminum interstitial ions, the electron radiation induced spectrum found was very similar to that reported for X- or  $\gamma$ -ray irradiated crystals. These bands, which saturated with dose, are accounted for by the presence of chromium<sup>+4</sup> ions and F-centers produced by the radiation. Probable ionization processes consistent with these findings and with those of other investigators are given.

## INTRODUCTION

The radiation induced degradation of the output of the ruby laser has stimulated new interest in the interaction of radiation with ruby and other ionic oxides. The more penetrating radiations, X-rays,  $\gamma$ -rays, electrons, and neutrons, are of more concern since these are known to cause extensive excitation and ionization of a rather permanent nature. For the higher energy radiations, displacement of crystal atoms may occur, leading to the production of lattice defects. Although there has been considerable and detailed study of color centers in the alkali halides, comparatively little attention has been given to the polyvalent ionic solids, including  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Cr<sub>2</sub>O<sub>3</sub>) (ruby). It is the purpose of this work to examine the nature of the centers produced in these oxides by various types of radiations. This will both contribute to the practical problem of laser development and, equally important, increase our general understanding of defects in this class of compounds.

In this study bombardments with 2-MeV electrons were made in an attempt to create additional defects by ion displacement. This is an extension of our previous investigations on ruby using X-ray irradiation (ref. 1). Optical anisotropy measurements of the observed optical spectra provided valuable insight into the nature of the centers produced by irradiation.

The effects of irradiation on corundum have been studied by many authors using optical absorption spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, and thermoluminescence. Corundum shows two main  $\gamma$ -ray induced optical bands at 3.1 and 5.4 eV, with perhaps another smaller band at 4.3 eV (ref. 2). Electron irradiation of corundum induces bands that are similar although less well defined (ref. 3). The anisotropies of these bands are all positive (i.e., the anisotropic ratio is greater than 1). The 3.1- and 5.4-eV bands, which saturate with dose, have been associated with holes or electrons trapped on preexisting lattice defects rather than with impurities (refs. 4 to 6). X-ray irradiation of corundum up to 300 kilovolts, however, did not produce any significant absorption bands in this region (ref. 1). With neutron bombardment, as with electron bombardment, additional defects are formed by displacement collisions. Several new bands occur. The strongest of these, at 6.1 eV, is believed to be due to electrons trapped on interstitial aluminum ions (ref. 3).

EPR spectra of  $\gamma$ -irradiated corundum indicate the presence of "hole-like" centers of spin 1/2 (ref. 6). Each center gives a single asymmetric line at 3.7 kilogauss ( $3.7 \times 10^{-4} \text{T}$ ). This is consistent with a hole trapped on oxygen ion adjacent to a positive ion vacancy ( $V_1$ -center). The F-center has also been observed, but it does not always show an EPR spectrum, because of a saturation effect.

In contrast, there has been relatively little investigation of the effects of radiation on ruby despite the serious degradation problem mentioned. However, in the few papers that have been published good agreement exists on the effects of high-energy electromagnetic radiation. Again, optical absorption spectroscopy, thermoluminescence, and EPR spectroscopy have been used to characterize the damage produced. The interpretation of these results for ruby, though, has found far less agreement. The centers produced by the radiation have not been clearly identified, and consequently details of the radiation damage process in ruby are not well understood.

In an earlier EPR investigation (ref. 1) we had detected chromium<sup>+4</sup> ( $\text{Cr}^{+4}$ ) ions in X-irradiated ruby. That work also suggested the presence of a V-center resonance at 3.7 kilogauss ( $3.7 \times 10^{-4} \text{T}$ ) in small concentration. Also in that report the optical spectrum was attributed to higher valence chromium ions, although no definite assignments of the bands were made. The possibility of  $\text{Cr}^{+2}$  being present was suggested but not detected.

Arkhangelskii, Morgenshtern, and Neustruev (ref. 7) also suggest both  $\text{Cr}^{+2}$  and  $\text{Cr}^{+4}$  being present in their irradiated ruby on the basis of thermoluminescence and electroluminescence which they believe to originate from transitions from the 2E level of  $\text{Cr}^{+3}$  ions.

Maruyama and Matsuda (ref. 4), on the other hand, ascribe their  $\gamma$ -ray induced spectrum to transitions on  $\text{Cr}^{+2}$ ,  $V_1$ , F, and other defect centers. Their spectrum agrees almost exactly with that which we found below 6 eV for X-ray irradiation and electron irradiation.

A similar absorption spectrum can also be seen in the unirradiated,  $\text{Cr}^{+4}$  doped,  $\alpha\text{-Al}_2\text{O}_3$  of Hoskins and Soffer (ref. 8). The striking similarity of this spectrum to those obtained after irradiation extends also to the anisotropy of the bands.

Despite the apparent disparity between the various investigators, we believe that with the findings of this work a simple interpretation of both our and their results is possible. This will be given in the DISCUSSION.

## EXPERIMENTAL

The ruby samples used were of laser quality and were prepared by Union Carbide Corporation, Linde Division. They were in all cases in the form of disks 3/8 inch (0.953 cm) in diameter and 1/16 inch (0.159 cm) thick. The C-axis was oriented to within a few degrees either  $0^\circ$  or  $90^\circ$  from the disk axis. The chromium content was nominally 0.05 percent. The samples were polished, and the orientation was marked for alinement purposes.

Irradiations were made with a commercial electron accelerator which produced a monochromatic beam of 2-MeV electrons. Some X-irradiations were made for comparison purposes using a commercial unit operated at 300 kilovolts and 8 milliamperes. The X-ray tube had a copper target and was equipped with a beryllium window.

All samples were irradiated in the dark at constant dose rate. During both types of irradiations the sample temperature was kept below  $75^\circ\text{C}$  except during one high dose electron run in which the temperature reached  $140^\circ\text{C}$ . There were no qualitative changes in the spectrum found for this higher temperature irradiation. The X-ray dose was recorded with a calibrated polystyrene ionization chamber; electron dose was determined using a Faraday cage and a current integrater.

All optical absorption data were obtained at room temperature using a double-beam recording spectrophotometer. The absorption spectrum from 6.2 to 1.9 eV (2000 to 6500 Å) was recorded for all determinations.

Polarization studies were done with two sets of sheet polarizers placed before the samples. The polarizers were transparent over nearly the entire spectral range studied except above 5.8 eV. The samples were rotated relative to the plane of polarization. The spectra in the form of optical density as a function of photon energy were analyzed with a commercial electronic curve fitter which resolves the spectrum into component gaussian bands. In most cases several samples were irradiated and analyzed for each experimental condition to establish clearly the validity of the effects seen.

## RESULTS

The optical absorption of ruby due to the electron irradiation was found by comparison of the irradiated crystal with an identical unirradiated crystal of similar orientation in a double beam spectrometer. A typical difference spectrum is shown in figure 1 with unpolarized light for purposes of comparison with previous data. It initially appeared that the data might be fitted by four peaks at approximately 2.6, 3.3, 4.3, and 6.0 eV. However, it was found that the region above 4.7 eV could not reasonably be fitted by a single gaussian but could be fitted quite well by two gaussians centered at about  $5.4 \pm 0.1$  eV and  $6.1 \pm 0.1$  eV. This is in some contrast to the difference spectrum obtained for X-irradiated ruby reported previously to have a single large peak in this region at 5.8 eV (ref. 1).  $\gamma$ -irradiated ruby also shows a similar peak at about 5.7 eV (ref. 4). In other respects the general shape of the induced absorption spectrum is very similar for these three types of radiation. There is also some arbitrariness to fitting the region from about 3 to 4 eV with a single peak. As will be seen, the polarized spectra indicate that the original single band fit is probably not correct.

It has been shown that the absorption due to X- and  $\gamma$ -irradiation saturated at about  $5 \times 10^5$  roentgens. For electron irradiated ruby the absorption also saturated over most of the spectral region. The optical density of the bands agreed remarkably well with those of X-irradiated samples.

For electron irradiated ruby, however, some difference is evident above 6 eV. The optical density was found to be relatively higher and was a function of dose. This can be seen in figure 2, which shows the ratio of optical density at 6.1 eV ( $\text{o.d.}_{6.1}$ ) to that at 4.3 eV and also the ratio for 2.6 to 4.3 eV as a function of radiation dose. The first ratio rises with increasing dose, whereas the second ratio remains relatively constant through saturation. While the 6.1-eV absorption did not appear to saturate with dose, an accurate growth rate cannot be determined because of the overlapping of the 5.4-eV peak and the proximity to the transmission cutoff of the spectrometer. The ranges of these ratios for X-irradiated ruby are also shown in figure 2 for comparison.

A series of furnace anneals was performed on a typical electron irradiated ruby specimen. Table I shows the bleaching due to successive 1-hour heatings at the given temperatures. Because of optical bleaching effects and lack of precise temperature control in the heating and cooling cycles, the actual annealing data are not precise enough for kinetic analysis. What is more significant is the relative annealing rates of the various spectral regions. Figure 3 shows the optical density ratios for spectral regions 6.1 and 4.3 eV, both relative to 2.6 eV, plotted as a function of annealing temperature. These ratios are calculated from the data in table I.

Up to 275° C the  $\frac{\text{o.d. 4.3}}{\text{o.d. 2.6}}$  ratio remains relatively unchanged, indicating a similar

annealing rate for both spectral regions. However, the  $\frac{\text{o.d. 6.1}}{\text{o.d. 2.6}}$  ratio increases sharply

above about 250° C, indicating that the 6.1 eV band anneals more slowly than do the other spectral regions. At slightly higher temperatures, the 6.1-eV band finally anneals out as well.

The anisotropy in the optical absorption in ruby after electron irradiation is shown in figure 4. Two curves are shown for absorption of light whose electric vector is parallel to ( $\parallel$ ) and perpendicular to ( $\perp$ ) the crystal C-axis. The shape of the curves generally agrees with that for the unpolarized spectrum of figure 1; the same peaks are indicated. In order to measure the anisotropy at the shortest wavelengths, it was necessary to anneal the sample slightly. This is shown as the lower curves in the 4- to 6-eV region.

Also shown is the spectrum of the anisotropic ratio  $\mathcal{A} = \frac{\text{o.d. } \parallel}{\text{o.d. } \perp}$ . The energy region

between 2 and 3.5 eV exhibits a negative anisotropic ratio ( $\mathcal{A} < 1$ ) with a peak at about 2.6 eV, coinciding with the optical density spectrum.

Another peak of negative anisotropy appears centered above 4.35 eV, corresponding exactly to the absorption peak at 4.35 eV.

A peak of positive anisotropy appears at about 3.8 eV. The corresponding peak in the absorption spectrum is not prominent; nevertheless, it suggests that the simple assignment of one band in the region between 3 and 4 eV may be in error.

A broad band of positive anisotropy occurs from about 4.9 to 5.8 eV, where the polarizers cut out.

Previous work on X-irradiated ruby (ref. 1) shows a loss of  $\text{Cr}^{+3}$  ion after irradiation. No change in the anisotropic ratio due to this loss would be expected since the ratio is independent of the amount of absorption, and thus the ratios for  $\text{Cr}^{+3}$  absorption before and after irradiation should cancel.

Shown also in figure 4 is the anisotropic ratio deduced from the data of Hoskins and Soffer (ref. 8). One curve is presented for the  $\text{Cr}^{+4}$  doped  $\alpha\text{-Al}_2\text{O}_3$  crystal and another for the same crystal after intense ultraviolet irradiation. These curves are discussed in the next section.

## DISCUSSION

The high-energy radiation induced optical absorption spectra of ruby and corundum are strikingly different. Though basically resulting from ionization and trapping processes in both materials, the trapping centers in corundum are primarily preexisting crystal defects (vacancies), while we conclude that most of the added coloration of ruby is related to ionization and transitions of the chromium impurity ions. Defect centers do contribute to the ultraviolet absorption spectrum of irradiated ruby; F-centers are produced with X-ray,  $\gamma$ -ray, and electron irradiation, and electron trapped interstitial aluminum ions with electron irradiation. But the  $V_1$ -center absorption so prominent in irradiated corundum is barely detected in irradiated ruby.

The findings of this work coupled with those of other investigators lead to a simplified picture of the radiation damage processes in ruby based on the identification of the peaks found in the optical absorption spectra and EPR spectra.

With ionizing irradiation, corundum shows two major bands at 3.1 and 5.4 eV. These have been ascribed to  $V_1$ -centers and F-centers, respectively (refs. 4 to 6). In contrast, figure 1 shows the optical absorption bands found in electron irradiated ruby. Prominent is the band found in common with  $\gamma$ -irradiated corundum at 5.4 eV, also of positive anisotropy. There is, however, no strong band of positive anisotropy observed in irradiated ruby at 3.1 eV. But, there are bands of negative anisotropy at 2.6 and 4.3 eV. Polarization data indicate a band of positive anisotropy at 3.8 eV. With electron irradiation an additional band at 6.1 eV of unknown anisotropy is indicated in our samples. We shall discuss this last band first since it has not been observed in irradiated ruby previously.

High-energy electron irradiation can, in addition to the usual ionization, cause displacement of the crystal atoms. The absorption at 6.1 eV is similar to the band observed in neutron irradiated  $\alpha$ - $\text{Al}_2\text{O}_3$ , ascribed to a center produced by trapping an electron on an interstitial aluminum ion (ref. 3). This and the fact that our 6.1 eV band does not saturate with dose further support the assignment of the 6.1 eV band to that defect center.

The other electron induced absorptions are identical to those found following X-ray (ref. 1) and  $\gamma$ -ray (ref. 4) irradiation of ruby. These bands do saturate with dose and therefore are not thought to be associated with displacement effects.

It is assumed that in ruby, as in irradiated corundum, the F-center absorbs at 5.4 eV, leaving then only the bands at 2.6, 3.8, and 4.3 eV to be accounted for. For reasons that follow we attribute these bands to crystal field excitation of  $\text{Cr}^{+4}$  ions. Chromium<sup>+4</sup> may also contribute to the absorption at 5.4 eV through charge-transfer transitions. The pertinent arguments leading to these assignments are the following:



(1) The absence, or low intensity of the 3.1 eV  $V_1$ -center band in irradiated ruby suggests that chromium in the  $\alpha\text{-Al}_2\text{O}_3$  crystal rather than the oxygen ion may preferentially ionize.

(2) The ratio of intensities of the bands reported in references 1, 4, and 8 and this work are quite similar. In all these studies the samples were prepared under quite different conditions with varying amounts of chromium and then annealed in various reducing and oxidizing atmospheres. This, coupled with the fact that the intensities of the bands all saturated with the same radiation dose (except the 6.1 eV band) and are proportional to the chromium concentration (ref. 4), makes it seem very unlikely that the bands could be associated with defect centers or with other impurities.

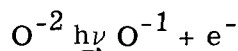
(3) All radiation induced bands are completely annealed out at about 300° C. This similar annealing behavior indicates a single (or interrelated) annealing process. However, Maruyama and Matsuda (ref. 4) have observed a slight increase in the intensity of the 5.4 eV band at about 200° C and a corresponding decrease in the band at 2.6 eV at the same temperature. Both bands anneal out completely at 300° C along with the other bands. This effect is more pronounced at lower chromium concentrations. The complex annealing of the 5.4- and 2.6-eV regions suggests a superposition of two bands in these regions, one of which anneals out at a lower temperature. Additional evidence for this point of view is seen in the glow curves of Maruyama and Matsuda. Two major peaks are observed corresponding in temperature to the annealing. The intensity of the second peak increases with chromium concentration. On the other hand, the first peak is relatively independent of chromium content, suggesting involvement of a defect center.

(4) Spectroscopically the  $\text{Cr}^{+4}$  ion is  $d^2$ . In  $\alpha\text{-Al}_2\text{O}_3$  the crystalline field is essentially octahedral with some trigonal distortion. The observed spectrum of vanadium<sup>+3</sup> ( $\text{V}^{+3}$ ) (also  $d^2$ ) in  $\alpha\text{-Al}_2\text{O}_3$  (ref. 9) was used to correct for the trigonal distortion of the  $d^2$  spectrum in an octahedral crystalline field, calculated by Tanabe and Sugano (ref. 10). The spectrum of  $\text{Cr}^{+4}$  was then calculated from this corrected diagram assuming appropriate values of the Racah parameters of  $Dq = 2070 \text{ centimeter}^{-1}$  and  $B = 1010 \text{ centimeter}^{-1}$ . The calculated spectrum of  $\text{Cr}^{+4}$  shows two major peaks in the region of 2 to 5 eV due to transitions  $3T_1 \rightarrow 3T_2$  and  $3T_1 \rightarrow 3T_1$  and a weaker absorption arising from  $3T_1 \rightarrow 3A_2$ . The theory predicts these bands at 2.6, 3.8, and 4.5 eV. The agreement with the observed radiation induced spectrum in ruby is very good even to the expected polarizations for these bands. The unusually high optical density of the spectral region above 4 eV, however, suggests contributions to the spectra of  $\text{V}^{+3}$  and  $\text{Cr}^{+4}$  from charge-transfer absorption.

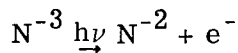
(5) The radiation induced spectrum in the region from 2 to 4.5 eV agrees remarkably well with that found by Hoskins and Soffer (ref. 8) for their  $\text{Cr}^{+4}$  doped  $\alpha\text{-Al}_2\text{O}_3$ . This similarity extends also to its anisotropy, which we have deduced from their data and show in figure 4. Hoskins and Soffer, however, did not ascribe their optical absorption bands

to  $\text{Cr}^{+4}$  on the basis that the optical absorption is destroyed by irradiation at 78 K with unfiltered ultraviolet light and is regenerated upon annealing at room temperature. (The anisotropy spectrum of figure 4, curve for irradiated  $\alpha\text{-Al}_2\text{O}_3$ , however, suggests that all of the  $\text{Cr}^{+4}$  may not be lost.) Their EPR data do not show the same reversibility on warming the ultraviolet irradiated sample to room temperature. However, their inability to observe the reverse reaction may have been due to the fact that the  $\text{Cr}^{+4}$  EPR line saturates strongly at higher temperatures. We could not detect it much above liquid nitrogen temperature. While admitting that  $\text{Cr}^{+4}$  would be expected to show optical absorption in this spectral region, Hoskins and Soffer chose rather to suggest that a doubly charged helium-like defect center gives rise to this absorption.

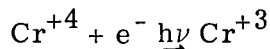
Consistent with our interpretation, we may also comment on the spectra observed by Hoskins and Soffer. We believe that the spectrum they observed prior to irradiation is due to  $\text{Cr}^{+4}$ . With strong ultraviolet irradiation the following reactions occur:



or



and



These reactions are reversible on heating to room temperature. Their 2.4-eV band of positive anisotropy observed after irradiation is probably due to  $\text{O}^{-1}$  or  $\text{N}^{-2}$ , perhaps adjacent to a positive ion vacancy.

The presence of a defect center contributing to the absorption in this region is not precluded, but, considering the strong arguments for  $\text{Cr}^{+4}$  absorption, there is no need to postulate it.

(6) Another suggestion that the 2.6 eV absorption be due to  $\text{Cr}^{+2}$  (ref. 4) also is doubtful since reasonable values of  $Dq = 1400 \text{ centimeter}^{-1}$  and  $B = 810 \text{ centimeter}^{-1}$  place this band near 1.8 eV, not at 2.6 eV. Furthermore, since the 2.6, 3.8, and 4.3 eV bands of Hoskins and Soffer are in exactly the same ratio as ours, this would require a similar ratio of  $\text{Cr}^{+2}/\text{Cr}^{+4}$  to exist in their samples as in ours. Because of the severe oxidizing conditions required in the preparation of their samples, it is extremely unlikely that their samples contain any  $\text{Cr}^{+2}$ . It is also expected by analogy with manganese ( $\text{Mn}^{+3}$ ) (ref. 9) that the  $\text{Cr}^{+2}$  band would be much weaker than the  $\text{Cr}^{+4}$  band in this region.

Arkhangelskii, Morgenshtern, and Neustruev (ref. 7) suggest that some absorption bands produced by low-energy optical irradiation of ruby may alternatively be due to  $\text{Cr}^{+2}$  ionization. However, this argument, based on a nonzero luminescence efficiency, is unambiguous only for their band at 3.3 eV. With our higher energy radiation we see no significant band at 3.3 eV. We do not, however, rule out  $\text{Cr}^{+2}$  being produced by irradiation; we just have no direct evidence for it, either from optical spectra or EPR.

## CONCLUSIONS

Based on the findings of this and prior work, we are led to the following tentative conclusions regarding the nature of the radiation damage in ruby.

As with corundum, there exist in ruby both positive and negative ion vacancies. These appear during the crystal growth process resulting from metal evaporation and subsequent loss of oxygen due to charge compensation. In irradiated corundum electrons excited from the oxygen valence bands are subsequently trapped at negative ion vacancies forming  $V_1$ -centers and F-centers:



The  $\text{O}^{-1}$  ion is stabilized if a positive ion vacancy is adjacent. This then is the  $V_1$ -center.

But in ruby the presence of chromium<sup>+3</sup> ( $\text{Cr}^{+3}$ ) markedly reduces the production of  $V_1$ -centers by preferential ionization of the  $\text{Cr}^{+3}$  ion:



With 2-MeV electron irradiation, displacement of aluminum<sup>+3</sup> ( $\text{Al}^{+3}$ ) ions and subsequent trapping of electrons will occur:



Other electron trapping reactions may also occur, including



In ruby, then, reaction (3) is established by EPR and optical absorption spectra of the  $\text{Cr}^{+4}$  ion. Reaction (1) is not as probable since no strong 3.1-eV optical band is observed. However, EPR confirms the presence of  $V_1$ -centers in small concentrations. Reaction (2) appears at least partially responsible for the optical band at 5.4 eV.

Charge transfer absorption of  $(\text{Cr}^{\text{IV}}\text{O}_4)^{-4}$  may also contribute in this region. Reaction (4) involving displacement collisions from electron bombardment is observed by absorption spectroscopy. Reaction (5) is suggested but is experimentally unverified in this work.

The model described represents a reasonable explanation for our experimental findings on the effect of irradiation on ruby. It is also consistent with the complementary findings of Maruyama and Matsuda, Arkhangelskii, Morgenshtern, and Neustruev, and Hoskins and Soffer, although not necessarily in agreement with their interpretations.

In conclusion, it appears from the experimental evidence that the major effect of high-energy radiation on ruby lasers will result from change in ionization of the chromium itself. Large effects have been observed on laser output and lasing threshold in irradiated ruby. A possible solution to the problem of degradation may be to deliberately dope the ruby with selected impurities which would preferentially ionize instead of the chromium.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, September 28, 1970,  
129-03.

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TABLE I. - EFFECT OF SUCCESSIVE 1-HOUR THERMAL ANNEALS  
ON COLORATION OF ELECTRON IRRADIATED RUBY SPECIMEN

Annealing temperature, °C	Optical density at 2.6 eV, o.d. 2.6	Optical density at 4.3 eV, o.d. 4.3	Optical density at 6.1 eV, o.d. 6.1	Optical density ratio	
				$\frac{\text{o.d. 4.3}}{\text{o.d. 2.6}}$	$\frac{\text{o.d. 6.1}}{\text{o.d. 2.6}}$
145	0.278	0.553	1.955	1.98	7.05
235	.170	.335	1.205	1.97	7.10
245	.096	.177	.751	1.84	7.82
255	.051	.100	.423	1.96	8.30
265	.026	.050	.250	1.92	9.32
275	.011	.021	.152	1.91	13.8

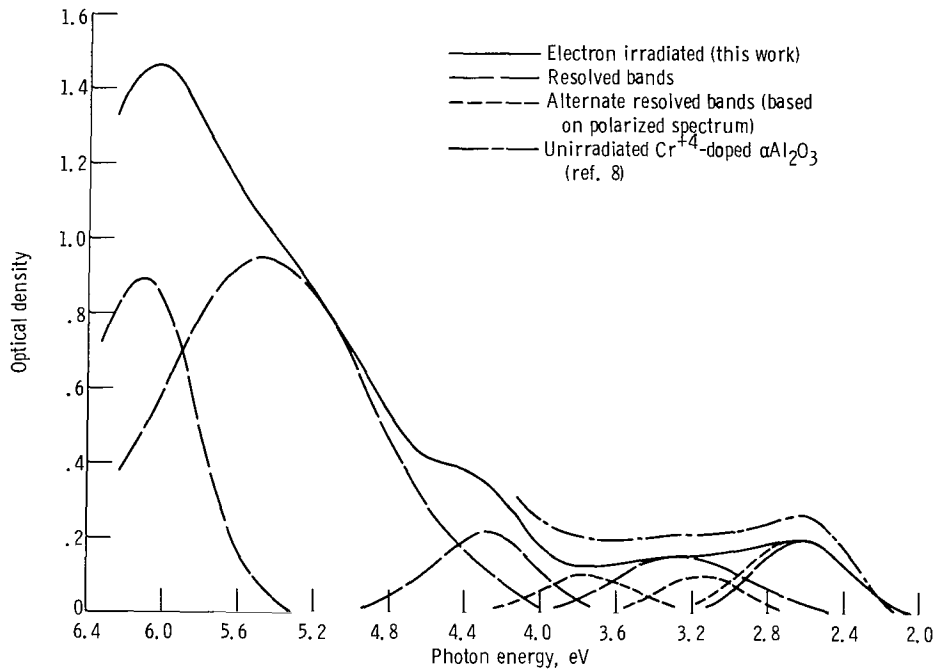


Figure 1. - Typical electron radiation induced absorption spectrum of ruby. Spectrum resolved into component bands.

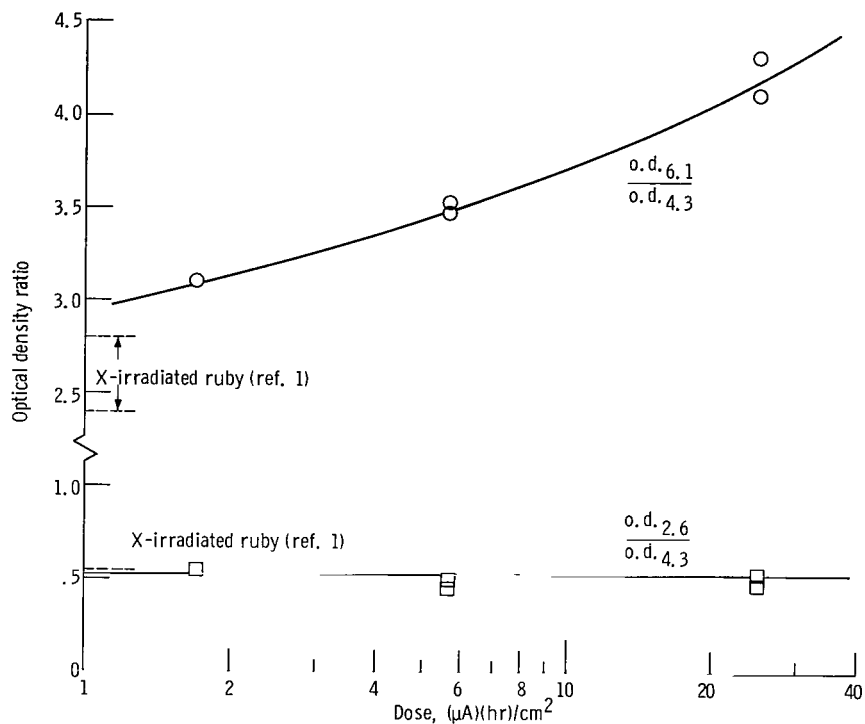


Figure 2. - Dose dependence of electron radiation induced optical density of ruby at 6.1 and 2.6 eV referred to density at 4.3 eV. (No dose dependence noted in data from ref. 1.)

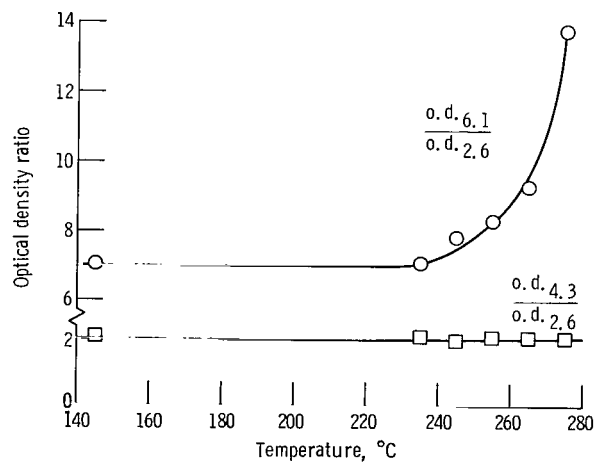


Figure 3. - Optical density ratios for spectral regions 6.1 and 4.3 eV, both relative to 2.6 eV, of electron irradiated ruby annealed at various temperatures.

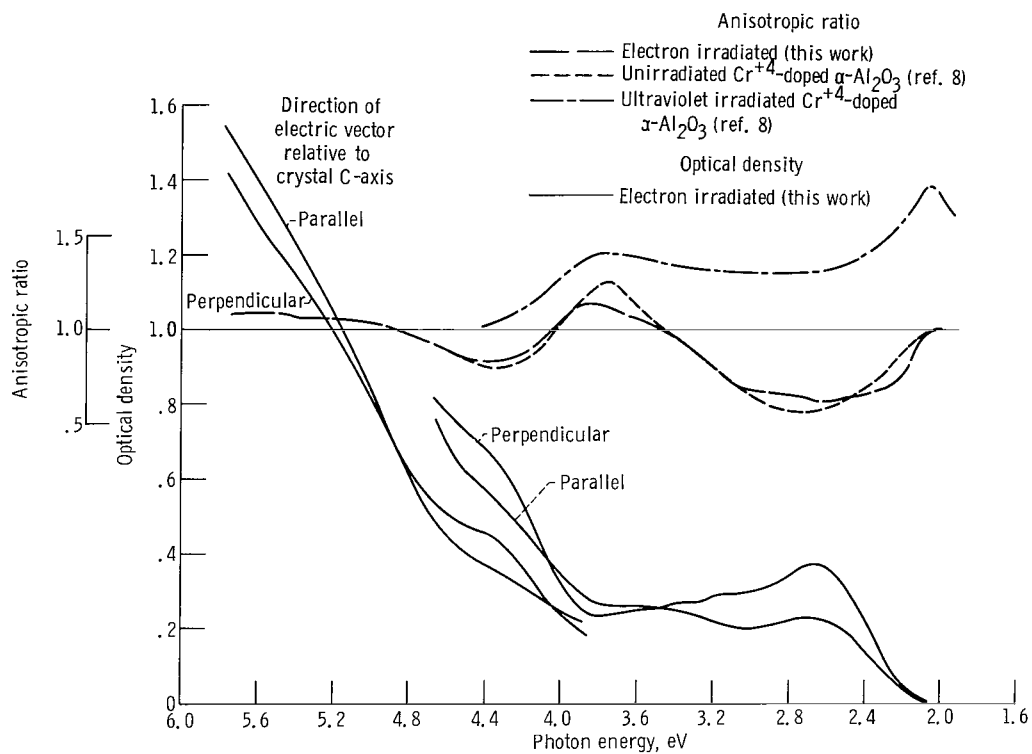


Figure 4. - Anisotropy of electron radiation induced optical absorption in ruby.



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